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Asymmetric membrane mfr. - based on 1-monoalkyl-dimethyl-silyl propyne polymer

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Patent Family:

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Patent Details:

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Abstract (Basic): JP 60132605 A

Method comprises using, as polymer, 1-monoalkyldimethylsilylpropyne polymer of formula (I) (where R is 1-4C alkyl) and tetrahydrofuran type organic solvent.

USE/ADVANTAGE - The asymmetric membrane is useful as a membrane of RO, UF, dialysis, gas-permeation and pervaporation. Conc. of the polymer in a dope is 0.1-30 wt.%, pref. 1-20 wt.%. The dope may be cast in this condition.

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Derwent Class: A26; A88; D15; J01

International Patent Class (Additional): B01D-013/04

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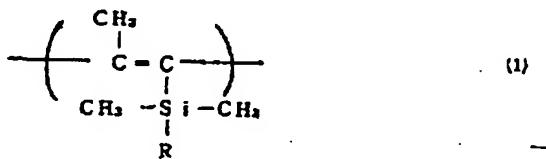
SPECIFICATION

1. TITLE OF THE INVENTION

PROCESS FOR PRODUCING ASYMMETRIC MEMBRANE

2. CLAIM

1. A process for producing a polymer asymmetric membrane, comprising introducing a dope that is composed of a solution of a polymer in an organic solvent into a coagulating bath to coagulate the dope, characterized by using, as at least part of the polymer, a 1-monoalkyldimethylsilylpropyne polymer having a repeating unit represented by the following general formula:



wherein R represents a C₁₋₄ alkyl group,

and, as the organic solvent, a solvent mainly composed of tetrahydrofuran or a derivative thereof.

2. The production process according to claim 1, wherein the polymer has a concentration in the dope of 1 to 20% by weight.

3. DETAILED DESCRIPTION OF THE INVENTION

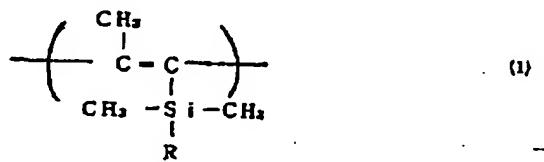
The present invention relates to a process for producing an asymmetric membrane. More particularly, the present invention relates to a process for producing an asymmetric membrane having good permeability and selectivity.

In recent years, membrane separation technology has attracted considerable attention as energy saving technology. And the technology ranges over many different separation membranes, including: for example, separation membranes for solution systems such as RO membranes (Reverse Osmosis membranes) used for desalination of seawater and UF membranes (Ultrafiltration membranes) useful for food processing; gas separation membranes such as oxygen enrichment membranes that enrich oxygen in air; and pervaporation membranes that are considered to be useful for separation of the water-ethanol mixture produced from biomass, which has been investigated for substitute fuel.

The present inventors have already found monoalkylsilylpropyne polymers to be raw materials for gas separation membranes and pervaporation membranes which have high permeability and filed an application for a patent on the process for producing an asymmetric membrane using such polymers (Japanese Patent Application Nos. 58-29736 and 58-186334). When using such a polymer to produce an asymmetric membrane, it is necessary to prepare a dope by dissolving the polymer in an organic solvent. And as organic solvents for such polymers, solvents of aromatic hydrocarbons, aliphatic hydrocarbons and halogenated hydrocarbons are reported by Higashimura et al. (Proceedings of the Society of Polymer Science, Japan, vol. 32, 6, 1175-1178). However, the asymmetric membranes produced using any one of these solvents have the disadvantages in that pinholes are more likely to form in the membranes and even in cases where pinholes do not form, such membranes do not have good selectivity when used as permselective membranes.

After directing tremendous research effort toward overcoming the above described disadvantages and toward obtaining an asymmetric membrane having high permselectivity, the present inventors have found that tetrahydrofuran is an excellent solvent for 1-monoalkyldimethylsilylpropyne polymers in the production of a highly permselective

asymmetric membrane, though it has never been reported as a solvent for 1-monoalkyldimethylsilylpropyne polymers. And the inventors have finally made the present invention. Specifically, the present invention is a process for producing a polymer asymmetric membrane, comprising introducing a dope that is composed of a solution of a polymer in an organic solvent into a coagulating bath to coagulate the dope, characterized by using, as at least part of the above polymer, a 1-monoalkyldimethylsilylpropyne polymer having a repeating unit represented by the following general formula:



wherein R represents a C₁₋₄ alkyl group,

and, as the organic solvent, a solvent mainly composed of tetrahydrofuran or a derivative thereof.

Examples of C₁₋₄ alkyl groups represented by R in the general formula (1) include: linear alkyl groups such as methyl, ethyl, propyl and butyl groups; and branched alkyl groups such as isobutyl and tert-butyl groups.

Examples of 1-monoalkyldimethylsilylpropynes which are used for obtaining the polymer having a repeating unit represented by the general formula (1) include: 1-trimethylsilylpropyne, 1-monoethyldimethylsilylpropyne, 1-mono-n-propyldimethylsilylpropyne, and 1-mono-n-butyldimethylsilylpropyne. Of these 1-monoalkyldimethylsilylpropynes, 1-trimethylsilylpropyne is preferable.

As 1-trimethylsilylpropyne, a commercially available monomer (a product from Petrarch, U.S., a product, T3728, from SP development department, Chisso Corporation) can be used.

The above described polymer can be obtained by polymerizing 1-trimethylsilylpropyne usually at 30°C to 100°C for 12 to 36 hours in the presence of a catalyst based on a Group V transition metal element, niobium (Nb) or tantalum (Ta), (such as NbCl₅, TaCl₅, NbBr₅, or TaBr₅), or in the presence of a solvent (such as an aromatic hydrocarbon such as benzene,

toluene or xylene, an aliphatic hydrocarbon such as cyclohexene, or a chlorine-based solvent such as 1,2-dichloroethane carbon tetrachloride). Alternatively, the polymer can be obtained by the method described in Japanese Patent Application No. 58-84626.

The polymer thus obtained is a white fibrous or powdery polymer. The number average molecular weight of the polymer, determined by light scattering, is usually 10000 or more and preferably 100000 or more.

The 1-monoalkyldimethylsilylpropyne polymer can be used in combination with another polymer, if necessary. Examples of other polymers applicable to the present invention include: 1-alkyne polymers (such as polymers of tert-butylacetylene, neopentylacetylene or tert-pentylacetylene, preferably tert-butylacetylene polymer); vinylorganosilane polymers (such as polymers of vinyltrimethylsilane, vinyltriethylsilane or vinyltripropylsilane, preferably vinyltrimethylsilane polymer); polyorganosiloxanes (such as dimethylsiloxane, polymethylphenylsiloxane and polydiphenylsiloxane); cellulose-based polymers (such as ethyl cellulose, hydroxyethyl cellulose and triacetyl cellulose, preferably ethyl cellulose); α -olefin-based polymers (such as polymers of 4-methylpentene-1); alkyl sulfone polymers (such as copolymers of α -olefin and SO_2 , preferably polymers of long-chain alkyl sulfone whose alkyl group has 10 to 20 carbon atoms); tertiary amine-containing polymers (such as vinylpyridine polymers, N,N-diethylaminoethyl acrylate polymers and N,N-dimethylaminostyrene polymers, preferably vinylpyridine polymers).

When the monoalkyldimethylsilylpropyne polymer is used in combination with a second ingredient (another polymer), the content of the monoalkyldimethylsilylpropyne polymer is usually 50% by weight or more and preferably 70% by weight or more on the basis of the total weight of the polymer used.

Examples of tetrahydrofuran and derivatives thereof that can constitute the organic solvent used to prepare the dope of the present invention include: tetrahydrofuran and alkyl substituted compounds of tetrahydrofuran (such as 2-methyltetrahydrofuran and 2,5-dimethyltetrahydrofuran). Of these compounds, tetrahydrofuran is preferable.

If necessary, another cyclic ether (such as pyran and dioxane), which is a compound similar to tetrahydrofuran, can also be used with tetrahydrofuran or a derivative thereof. The content of tetrahydrofuran or a derivative thereof in the above described organic solvent is usually 50% by weight or more and preferably 70% by weight or more.

In the production of an asymmetric membrane, another substance is often added to accelerate phase separation or adjust the solubility of polymer.

As such a membrane formation adjuster, a compound can be used which has compatibility as high as 0.1% or more with the dope of the polymer.

As the adjustor, not only solvents for the polymer, such as aliphatic hydrocarbons (such as petroleum ether and hexane), aromatic hydrocarbons (such as toluene and xylene) and halogenated hydrocarbons (such as carbon tetrachloride and chloromethyl), but also inorganic salts soluble in the dope, such as inorganic acid (such as hydrochloric acid and perchloric acid) salts of alkaline metals (such as lithium chloride and lithium perchloride), can be used. Water, lower alcohols (such as methanol and ethanol), and polyethylene glycol can also be used.

The concentration (weight) of the polymer in the membrane forming dope is usually 0.1 to 80% by weight and preferably 1 to 20% by weight. If the polymer concentration is less than 0.1% by weight, an asymmetric membrane having sufficient strength cannot be obtained, while if the concentration is more than 30% by weight, the dope solution has so high viscosity that it does not have sufficient spreadability when undergoing casting.

The amount of the membrane forming adjustor or additives in the dope solution varies depending on the solvent used in the membrane forming solution or the concentration of the polymer in the same. When the additives used act as an inflating agent or solvent, the amount of the additives is usually 10% by weight per 100% of the polymer to several ten times the weight of the polymer. For the additive such as an inorganic salt, the amount is 0.1% by weight to 200% by weight per 100% of the polymer.

The viscosity of the dope solution is usually 5 to 1000 poise, but it varies depending on the polymerization degree of the polymer or the kind of the adjustor used.

The dope solution thus produced is formed into a sheet, tubular or hollow-fiber membrane by cast coating the solution onto a substrate whose surface is smooth, for example, onto a sheet substrate or a tubular substrate made of a material such as glass, stainless steel, aluminum, polyethylene or polypropylene, or by extruding the solution through a ferrule having an annular orifice so that the solution takes the form of a hollow fiber. The dope solution can sometimes be directly cast and coated onto a substrate, for example, onto a woven fabric or nonwoven fabric made of an organic fiber such as a polyester, nylon or acrylic fiber or made of an inorganic fiber such as a glass fiber to form a composite asymmetric membrane.

The thickness of the coating in the present invention is adjusted to 10 to 1000 μ and preferably 50 to 700 μ . The thickness of the asymmetric membrane obtained varies depending on the concentration, evaporation time or temperature of the dope used, even if the thickness of the coating is made same.

In some cases, the dope is brought into contact with a coagulating medium and gelatinized right after being cast onto a substrate. However, generally it is gelatinized after part of the solvent is evaporated so that a very thin dense layer is formed on the surface of the membrane. The temperature and time of evaporation of the solvent vary depending on the kind of the solvent or the intended membrane performance; however, generally the evaporation is carried out at between -50°C and 100°C for between 0 and several ten minutes. As the gelatinizing solution (or the coagulating bath), a solution that is a non-solvent for the polymer, but compatible with tetrahydrofuran, such as water, methanol, ethanol, acetone, an inorganic salt aqueous solution or a mixed solution thereof, is used. Of these solutions, water is preferable.

The operation of gelatinizing the membrane is usually carried out at temperatures lower than the boiling point of the gelatinizing medium. For example, when the gelatinizing medium is water, the operation is usually carried out at 0 to 80°C. The time required for the gelatinization is usually several minutes to several hours, though it varies depending on the gelatinizing temperature. After the gelatinization, the membrane is immersed in running water about 24 hours so that the solvent or additive remaining in the membrane is washed out.

Depending on the situation, the membrane is immersed in an organic medium such as alcohol and then washed in running water.

The permeable membrane obtained as above is an asymmetric membrane made up of: a dense skin layer which forms the membrane surface; and a porous layer which forms the sublayer.

In the present invention, the performance of the asymmetric membrane obtained as above can be adjusted, if necessary, by subjecting the membrane to heat treatment in a medium such as water, ethylene glycol or saline solution. The treatment temperature is preferably between 50°C and 150°C and the treatment time is preferably between several minutes and several hours.

The resultant asymmetric membrane which has a desired performance can be used as a RO membrane, UF membrane, dialysis membrane, gas separation membrane or pervaporation membrane.

When using the asymmetric membrane obtained as above as a gas separation membrane, the membrane needs to be used as a dried membrane.

Methods of obtaining such a dried membrane (particularly when gelatinizing operation is performed in water) include: for example, a. freeze-drying the membrane; b. subjecting the membrane to solvent replacement with a water-miscible organic solvent and, if necessary, to solvent replacement with a nonpolar organic solvent as well; and c. simply air drying, breeze drying or vacuum drying the membrane. In the method b, solvents such as C₁₋₄ alcohols, glycol or ketone-based solvents, which are more likely to replace water in the wet membrane and have a low melting point, are preferably used as a water-miscible organic solvent. As a nonpolar organic solvent, ether or the like can be used. In the method c, where the membrane is simply air dried, breeze dried or vacuum dried, the drying may be carried out at ordinary temperature or under heat.

The present invention is a process for producing an excellent permselective asymmetric membrane using polymer including a 1-monoalkyldimethylsilylpropyne polymer.

In the following the present invention will be described in more detail by several examples. It is to be noted that these examples are not intended to limit the present invention.

Examples 1 to 8

1-Trimethylsilylpropane polymer (hereinafter referred to as PMSP) (the intrinsic viscosity of PMSP is 6.9 in toluene at 80°C) alone or a mixture of PMSP with another polymer is dissolved in a solvent mainly composed of tetrahydrofuran solution at a given concentration to prepare a dope solution.

The dope was cast onto a glass sheet using a 500- μ applicator, allowed to stand at room temperature so that part of the solvent was evaporated, and introduced into a gelatinizing bath having been adjusted to a given temperature so that the membrane was gelatinized. The gelatinized membrane was immersed in running water and allowed to stand there overnight so as to completely remove the solvent remaining in the membrane. The resultant asymmetric membrane was flexible and looked milk white on the outside. The membrane forming conditions and the results (membrane thickness) are shown in Table 1.

Example 9

The asymmetric membranes formed in Examples 2 and 5 were immersed in methanol and air-dried to prepare dried membranes. The evaluation of the gas permeability (oxygen, nitrogen) of each membrane was as shown in Table 2.

Example 10

Pervaporation experiment

Pervaporation separation experiment was carried out using the membrane of Example 2.

As the object of pervaporation separation (water-organic liquid mixture), a solution of 10% (by weight) ethanol in water was used. As an apparatus used was flat membrane-type ultrafiltration equipment (including a magnetic stirrer in the cell) having an effective membrane diameter of 45 mm, manufactured by Toyo Kagaku Sangyo, which was directly connected with a vacuum line. The permeation experiment was carried out at 25°C. The vacuum degree was 1.0 Torr and the permeate was trapped with a trap having been cooled with liquid nitrogen. The

flow rate ($\text{kg/m}^2\cdot\text{h}$) was calculated by collecting the permeate for a predetermined period of time. The concentration of organic matter in the permeate was determined by gas chromatography. The results are shown below.

Permeate flow rate $12.8 \text{ kg/m}^2\cdot\text{h}$

Permeate ethanol 64%

Table 1

	Polymer other than PMSP	PMSP/polymer ratio (by weight)	Adjustor	Concentration of adjustor in THF (% by weight)	Concentration of all the polymers in dope (% by weight)	Dope temperature (°C)	Evaporation time (sec)	Gelatinizing bath temperature (°C)	Membrane thickness (μ)
1	-	-	-	-	2.5	10	2	0	80
2	-	-	LiClO ₄	2.0	5.0	10	2	0	45
3	-	-	Water	2.0	2.5	10	2	20	25
4	-	-	Methanol	2.0	5.0	10	0	0	42
5	PVMS ¹⁾	7:3	-	-	5.0	10	0	0	38
6	PVMS	7:3	-	-	5.0	10	10	0	86
7	PTBA ²⁾	7:3	-	-	2.5	10	0	0	28
8	PTBA	7:3	-	-	2.5	10	10	20	26

1) polyvinyl trimethylsilane
 2) tert-butylacetylene polymer

Table 2

	Example 2	Example 5
P(O ₂) cm ³ (STP)/cm ² ·sec·cm	8.6×10 ⁻³	4.1×10 ⁻³
P(N ₂) cm ³ (STP)/cm ² ·sec·cm	4.1×10 ⁻³	1.4×10 ⁻³